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(54) Tide: FAT BLENDS CONTAINING DIGLYCERIDES

(57) Abstract

Fat-blends suitable for food applications, comprise blends of: 10-60 % diglycerides (=A), 90-40 % triglycerides (=B) wherein (A) contains \geq 70 % SU-diglycerides, including high melting diglycerides (> 40 °C) (=C) and simultaneously a fairy compound (D) so that the melting point of (C+D) is \geq 5 °C, lower than the melting point of (C) wherein (B) has an N₅ \leq 40 while the total blend has a SAFA-content of (C+D) is \geq 5 °C, lower than the melting point of (C) wherein (B) has an N₅ \leq 40 while the total blend has a SAFA-content < 40 %.

> / DG 10-60 Y. SO. PO DG 5時代 TG 90-40 Y. カロ・フロンジニ MP. 40°C以EのATA

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Fat blends containing diglycerides

In the prior art many fatblends have been disclosed, that are suitable for fat-containing food products, such as:

5 confectionery products, fillings, cream alternatives, bakery products, cheese, margarines and spreads. In order to be applicable in each of these applications the fats must fulfil a number of criteria, such as

- they must have a critical plastic consistency, both at refrigeration and at ambient temperature (spreads)
 - they must be melting readily and completely in the mouth (for all applications)
- and nowadays also: they preferably should be healthy
 (for all applications).

In order to meet the above requirements the fats must have a specific N-profile (solid fat index at different temperatures), while the fats also must have a specific fatty acid composition (i.e.: its FAME).

- solutions for the above problem were found for fats based substantially on triglycerides. In most of these fats a structuring compound of the trisaturated type (i.e.: S₃, S=saturated fatty acid) or a trans-fat had to be present.
- 25 However, the presence of these triglycerides S, or transrich triglycerides is not very beneficial for its healthy character, because it will cause a relatively high level of saturated or trans fatty acids in the fats, which saturated acids are believed to be responsible for heart- and
- vascular diseases. Therefore, a solution was sought in another direction. In WO 91/08677 a margarine oil is disclosed, that is low in trans fatty acids and low in intermediate chain saturated fatty acids (including C16:0) and wherein as a structuring fat 5-15 wt% of fatty acid
- 35 diglycerides are present. So, the above fats comprise:
 - 84 95 wt% triglycerides
 - 5 15 wt% diglycerides

< 3 wt% trans-acids

< 6 wt% intermediate chain fatty acids

25 - 45 wt% C_{18:2}

5 0 - 11 wt% C_{18:3}

5 - 25 Wt% C18:1

while the fatty acid residues are non-random distributed, and the fatblend displays a solid fat profile of:

 $N_{10} = 7 - 31$

10 $N_{21} = 3 - 25$

 $N_{27} = 0.7 - 10$

 $N_{33} = 0.5 - 4$

 $N_{39} < 3$

The fatty acid composition of the diglycerides is not disclosed. However, from the examples it can be concluded that the diglycerides will be rich in UU-diglycerides, $U=C_{18:1}$ and $C_{18:2}$.

From the above composition it can be calculated that the
fats have a theoretically minimum SAFA-content of 37 wt%.

Moreover, the requirement for the non-random distribution
causes, that the fats can only be obtained along an enzymic
route using directing (1.3-specific) enzymes. The
diglyceride-content is obtained by adjusting the water
content during the enzymic conversion to levels that
produce the required amount of 5-15 wt% of diglycerides.

Therefore, the above document does not provide a solution for fats with SAFA-contents below 37 wt%, wherein the fatty acids do not need to be present in a non-randomized way and that can contain higher amounts of diglycerides.

From EP 417 562 fat continuous emulsion are known, having an oil phase and a waterphase in a ratio of 99:1 to 5:95. The oil phase comprises a diglyceride mixture, which is not specified. According to reference example 2 the diglyceride mixture can be obtained by a conversion of glycerine with

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rapeseed oil in the presence of Ca(OH)₂. The product obtained contained 19,4% triglyceride and 79,6 wt% of diglyceride. This mixture was mixed with refined rapeseed oil. Similar oil products could be obtained by starting from palm oil and lard. In order to be able to make fatcontinuous emulsions from these mixtures a phospholipid mixture comprising N-free phospholipid and N-containing phospholipid had to be used in a weight-ratio of at least 1,0. Nothing is disclosed about the role of the diglycerides, nor about a lowering of the melting point(s) of higher melting diglycerides.

From EP 378 893 oil/fat-compositions are known, comprising a diglyceride-containing glyceride mixture and a phospholipid with a specific composition. The fats are resistant against oxidation and can be used as cooking, deep frying, pan frying, roasting or baking fat. The oil can contain 5-100% of diglycerides. The fatty acid residues can have a chain length of 8-24 C-atoms, while the content of unsaturated fatty acid residues is up to 70 wt%. The 20 content of SU-diglycerides is up to 40%, the content of SSdiglycerides is up to 5%; the rest being UU-diglycerides. So its content of UU-diglycerides is very high. The glyceride mixture can be obtained by an enzymic conversion of glycerol with an oil high in unsaturated fatty acid residues. Nothing is disclosed about fats having a diglyceride-component with ≥ 70 wt% SU-diglyceride, which simultaneously contains another component, that decreases the melting point of high melting diglyceride SU.

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According to EP 425 958 oil-in-water-in oil emulsions are obtained having on total fat 10-100% of a diglyceride with a melting point below 20°C.

35 In EP 171 112 edible fat compositions are disclosed that contain 5-30 wt% diglycerides. In the mixtures specific ratios between diglycerides and monoglycerides must be

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fulfilled, while the level of saturated fatty acids with 16-22 C-atoms in the diglycerides is kept below 45 wt%. According to the specification, the diglycerides have a profound influence on the crystallisation behaviour of fats and have a beneficial effect on the spreadability of hard fats. The diglycerides, therefore, are not used in order to achieve a structuring of the fats; for this purpose quite a high amount of hardened fats are present in the fat blends (according to all examples). As a result of the above the SAFA-level of the total fat blend is still quite high. Moreover, the presence of high melting diglycerides, such as Sto or Po, i.e. with a melting point above 40°C, particularly when present in high amounts, will cause problems with the oral response.

- We have studied, whether we could find fat blends, wherein the higher melting diglycerides could be present, whereas their oral response was still good. This study has resulted in the novel fat blends according to our invention. So, our invention concerns fat blends, comprising:
- 10-60 wt%; preferably 30-55 wt% of diglycerides (= A) and 90-40 wt% of triglycerides (= B), wherein (A) contains at least 70 wt% of diglycerides of the SU-type (S= saturated fatty acid C_{12} - C_{24} ; U= unsaturated fatty acid C_{16} +), including high melting diglycerides (= C) with a melting point above
- 40°C, while (A) simultaneously contains at least one other fatty component (D), which fatty component (D) is selected, so that the melting point of the mixture (C+D) is at least 5°C less than the melting point of component (C), and wherein the triglyceride component (B) has a solid fat
- content (NMR-pulse, not stabilised) at 5°C of at most 40 ($N_5 \le 40$), preferably at most 25, most preferably at most 15, while the total blend has a content of saturated fatty acids (= SAFA) of less than 40 wt%, preferably < 30 wt% and an N_{35} < 15.

In the above fat blends the higher melting diglyceride (C) is preferably StO or PO (St= stearic; P= palmitic;

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O= oleic). These higher melting diglycerides are preferably present in amounts of at least 5 wt%, in particular at least 10 wt% (on diglycerides). However, other diglycerides, such as BO or AO, are also applicable (B=behenic; A=arachidic).

This new finding is based upon the finding that certain mixtures of diglycerides or mixtures of a diglyceride and a triglyceride display a melting point that is lower than the melting point of the higher melting diglyceride. Therefore, 10 diglycerides with a relatively high melting point, which would make them unsuitable for food applications can still be used in these foods, however, only when combined with another fatty component, such as another diglyceride or triglyceride. This enables us to take advantage of the structuring properties of these diglycerides, while the oral response of the fats is also good, because of the lowered melting point of the mixture. The effect can be illustrated by the attached figure I. Herein the melting points of mixtures of PO and SO (P= $C_{16:0}$; S= $C_{18:0}$; O= $C_{18:1}$) as

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20 a function of the PO-content (as obtained by DSC) are given. It can be concluded that the melting point of StO is about 48.5°C and that the melting point of PO is about 41°C, whereas the melting point of a mixture of StO and PO is lower than the melting point of the higher melting StO.

Although the above effect can also be obtained for mixtures of a diglyceride and a triglyceride, we prefer to apply mixtures of two different diglycerides, so that the melting point of the mixture of the higher melting SU and the other fatty component preferably is 30-45°C, most preferably 32-40°C.

The mixture of diglycerides (A) that can be used can contain diglycerides of the SS- and SU-type. This means, 35 that they can contain simultaneously one or two saturated fatty acid residues S with 12-24 C-atoms and one or two unsaturated fatty acid residues with at least 16 C-atoms.

The exact position of the residues S and U is not very important. Still we have a preference for the use of 1.3-diglycerides as they have slightly better structuring properties. So, e.g. 1S-2U-diglycerides are as suitable as 1S-3U diglycerides or as 1U-2S-diglycerides. However, we prefer to apply a mixture with a very high content of diglycerides of the type SU, in particular diglycerides with one oleic and with one palmitic acid residue and diglycerides with one oleic and one stearic acid residue.

These diglycerides can be present in weight ratios of 5:95 - 95:5, preferably 20:80 - 80:20.

Our compositions can be made by blending of mixtures of diglycerides, rich in the required diglycerides with triglycerides, in particular liquid triglycerides, such as sunflower oil, olive oil, maize oil, soybean oil, rapeseed oil etc.

The diglycerides can be obtained according to many methods, such as:

- 20 1. hydrolysis of triglycerides, this hydrolysis can be performed along a chemical route (using a base) or along an enzymic route.
- interesterification of glycerol with a triglyceride or an acid. Again a chemical or an enzymic route can be applied.

The starting fatty material for the interesterification with glycerol preferably has a high S_2U -content (> 40%, in particular > 50%). A convenient enzymic route using glycerol and an acid is disclosed in e.g. EP 307,154. In general, the crude products obtained by those routes need to be purified, e.g. removal of monoglycerides by distillation, followed by fractionation.

35 The above blends can be free of trans acids and free of chemically interesterified fats. However, blends that contain chemically interesterified fat-component can also

be applied (either per se or in combination with nonchemically interesterified fats).

Although the triglyceride-component of our blends can be 5 selected from a broad range of triglycerides, provided that the total composition meet our SAFA-requirement (< 40%), we prefer to use fats with an N₅ ≤ 40 as our triglyceridesource. Components of those fats are suitably selected from the group consisting of sunflower oil; soybean oil; safflower oil, olive oil, high oleic sunflower oil, maize oil, high oleic safflower oil and olein fractions of vegetable oils, such as palm oil. It is, however, also possible to use fats obtained by enzymic conversion, or olein-fractions obtainable by fractionation (wet- or dry) of enzymically made oils. 15 The enzymic conversions can be performed using the technology disclosed in our GB 1,577,953. The starting materials should be selected such, that the desired fats or oils are obtained. It is, of course, also possible to use fats that are made according to chemical 20 interesterification-processes (with or without a

Food products that can be made comprise filling fats,
enrobed filling fats, confectionery products, wrapper
spreads, wrapper margarines, wrapper shortenings, tub
spreads, tub margarines, cream alternatives, bakery
products, doughs, cheese, mayonnaise and dressings.
Each of these food products comprise a fat phase and this
fat phase then consists at least partly of the novel fats
according to the invention.

fractionation step).

It should be understood that for each application the fat blends require a specific N-line. Briefly, it can be said that the following N-requirements must be fulfilled for the application indicated:

	filling fat	$N_5 > 50$	į	N ₃₅ < 8
	tub spread	$N_5 = 30 - 35$;	$N_{35} < 5$
	wrapper spread	N ₅ = 38-45	;	$N_{35} < 5$
	bakery products	$N_5 > 45$;	$N_{35} < 8$
5	cream alternatives	$N_5 \approx 30$;	$N_{35} < 5$
	confectionery produc-	ts N, > 80	;	N ₃₅ < 8

EXAMPLES

A mixture of palm oil-midfraction, glycerol and 1.1 lipolase 100 L-enzyme @ (ex NOVO-Nordisk) was converted in a weight-ratio of 100:20:1. The pH was 5 kept at 7,0, using a phosphate buffer. The conversion was performed at 35°C for 24 hours under stirring. Excess glycerol was decanted off. Monoglycerides and free fatty acids were removed from the crude 10 reaction product (containing 38,6 wt% of diglycerides and 33,7 wt% of monoglyceride) in a falling film evaporator at 260°C and 0,3 mm Hg: The product contained 47,8 wt% of diglycerides and 2,1 wt% of monoglycerides. 15 The product was bleached and deodorised and fractionated from hexane (1,5:1 hexane to oil ratio at 30°C). The olein was collected (yield 78%) and contained 45,6 wt% of diglycerides. In a second hexane fractionation, above olein-20 fraction was fractionated, (3,22 : 1 hexane to oil ratio at -10°C); a stearin fraction was obtained. This stearin fraction contained 60 wt% of diglycerides of which 56,7 wt% were of the SU-type. The overall yield from fractionations was 29%. A 25 third fractionation was performed on the stearin fraction obtained (5:1 hexane to oil at 24,5°C). The olein-fraction was collected, it contained 62 wt% of diglycerides of which 72,5 wt% were SUdiglycerides. The overall yield was 23%. 30 Excess monoglycerides was removed from the final olein-fraction via a silica-treatment with hexane/acetone (88:12) as solvent (5:1:0,78 = solvent : oil : silica). The product was washed with solvent. The resulting product was rich in PO (P = 35 $C_{16:0}$ O = $C_{18:1}$) and contained 61,4 % diglycerides and 0,0 % monoglycerides.

The diglycerides consisted of 25% SS; 70,7 % SU and 4,2 % UU.

Its fatty acid composition was:

F.F.A.-residue 14:0 16:0 16:1 18:0 18:1 18:2 18:3 20 0,4 50 0,0 7,3 39,3 2,1 0,0 0,6

1.2 Shea-stearin, glycerol, lipolase 100 L @ (ex Novo-Nordisk) were mixed in a weight-ratio of 100:20:1.

The pH was adjusted at 7.0 using a phosphate buffer.

The conversion was performed at 40°C during 8 hours under stirring.

Excess glycerol was decanted off. Monoglycerides and free fatty acids were removed (falling film evaporator 260°C, 0,3 mm Hg).

The resulting product was fractionated from hexane (3:1 hexane : oil; 21°C). An olein fraction was collected (yield 96% : diglyceride content 22,5 wt%).

In a second hexane-fractionation above olein fraction was fractionated (6,65: 1 hexane: oil at -7°C), the stearin-fraction was collected (18% diglyceride of which 72,6% SU-type). Overall yield 60%. The product was refined by a two-stage silicatreatment. Diglycerides and monoglycerides were adsorbed onto silica (hexane as solvent; ratio hexane: oil: silica = 2:1:1,22). The silicacomplex was washed with hexane and the wash was discarded.

The silica-complex was washed with hexane/acetone (88/12) in ratio 3,5 wash : 1 oil.

The wash was collected. The solvents were removed. The resulting oil contained 46.8 w t% diglyceride and 0.0 % monoglyceride. It's composition was 22% SS, 73.6% SU and 4.4% UU.

The fatty acid composition of the diglycerides was: F.F.A.-residue 14:0 16:0 16:1 18:0 16:1 18:2 18:3 20 0,4 2,3 0,0 57,4 35,9 2,1 0,0 1,9

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A blend was made from sunflower oil, the PO-rich products from example 1.1 and the StO-rich product from example 1.2 (ratio: 71:14,5:14,5). The blend contained 19,6 % diglycerides. The diglyceride-composition was: 21,2 % SS, 70,3 % SU and 8,4 % UU. The fatty acid composition of the total blend was: F.F.A.-residue 14:0 16:0 16:1 18:0 18:1 18:2 18:3 20 0,2 12,6 0,1 12,5 26,6 46,5 0,0 0,6 Total SAFA: 27,7 wt%.

Solid fat index (NMR-pulse: not stabilised).

<u>°C</u>	<u> </u>		
10	18,3		
30	3,4		
35	3,0		

2. Preparation of spreads

2.1 40% Fat Spread

a. Formulation

Fat Phase

Fat blend of example 1.3	40	₹
Hymono 7804 (Monoglyceride : IV = 80)	0,3	ષ્ટ્ર
Colour (B-carotene)	0,0	18
Flavour	0,1	ફ
Total ·	40,4	1%

Aqueous Phase (to pH 5.1)

Water	56, 5 %
Skimmed Milk Powder	1,5 %
Gelatin (270 bloom)	1,5 %
Potassium Sorbate	0,15%
citric Acid Powder	0,07%

All percentages on product basis.

b. Processing

The processing was performed on a microvotator, comprising an ACAC-set up.

3 kg of material was prepared and processed. The microvotator processing line was set up as follows:

follows:

Premix condition - Stirrer speed 100 rpm

- Temperature 50°C

Pump - Proportioning pump set at 80% (40.3 g/min).

A₁ conditions - Shaft speed 1000 rpm

Temperature set at 10°C

C, conditions - Shaft speed 1000 rpm

Temperature set to 13°C

A conditions - Shaft speed 1000 rpm

Temperature set to 12°C

C₂ conditions - Shaft speed 1000 rpm

Temperature set to 15°C

The aqueous phase was prepared by heating the required amount of water to approximately 80°C and then, using a Silverson mixer, slowly mixing in the ingredients. The pH of the system was adjusted to 5.1 by adding 20% lactic acid solution as required.

A premix was prepared by stirring the fat phase in the premix tank and then slowly adding in the aqueous phase. When addition was complete, the mix was stirred for a further 5 minutes before pumping through the line. When the process had stabilised (around 20 minutes), product was collected for storage and evaluation.

Typical exit temperatures from the units were:

A1 15,0°C

C1 17,1°C

A2 16,5°C

C2 16,6°C

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c. Evaluations

Products were collected from both of the C-units. Very good oil continuous low fat spreads were produced using this system. Hardness C and conductivity of the products were measured.

Product (40% fat)	C-value @ 5°C (gcm²)	C-value @ 20°C (gcm²)	Conductivity @ 5°C (uScm ⁻¹)	Conductivity @ 20°C (µScm ⁻¹)
ex C _i	1180	190	10⁴	10-4
ex C ₂	1400	210	10⁴	10⁴

All products had a good oral melt down and were fat-continuous.

2.2 80% Fat Spread

a. Formulation

Fat Phase

Fat blend of example 1.3	80 동
Hymono 7804	0,3 %
Flavour	0,1 %
Colour (ß-carotene)	0,01%

Aqueous Phase (to pH 5.1)

Water	18,3 %
Gelatin (270 bloom)	0,5 %
Skimmed Milk Powder	0,5 %
Potassium Sorbate	0,05 %
Citric Acid Powder	0,025%

All percentages on product basis.

b. Processing

Identical conditions were used for the preparation and processing as for the 40% fat spread.

Exit temperatures for this run were typically:

A1 15,3°C

C1 15,9°C

A2 15,7°C

C2 15,6°C

As before, oil continuous product could successfully be obtained at any point after C-unit 1.

Product was collected ex C1 and C2 for storage and evaluation.

c. Evaluation

Product (80% fat)	C-value @ 5°C (gcm²)	C-value @ 20°C (gcm²)	Conductivity @ 5°C (µ5cm ¹)	Conductivity @ 20°C (µ8cm¹)
ex C ₁	1820	200	10 ^{4.}	10 ^{.5}
ex C,	2100	180	10-3	103

All products were oil continuous with a good oral melt-down.

3. Preparation of a filling

Recipes

Fillings were made according to the following recipe:

	<u>- %</u>
Sugar	45
Cocoa powder N-11-N	7
Skimmed milk powder	10
Fat	3.8
Lecithin	0,5

The fats used were:

- 1. Blend of an interestified fat and palm oil olein in ratio 5:95, known as Biscuitine SF $\ensuremath{\Phi}$
- 2. Fat of example 1.3.

The SAFA content of the fats was:

1. Biscuitine SF : 40 %

2. Fat example 1.3 : 27,7%

The fillings were made using a Hobart mixer, Bühler refiner and Pascal conche.

Evaluation

Filling 1 was cooled to 22.5°C and filling 2 was cooled to 19.5°C, before they were piped into aluminum cups. The aluminum cups were stored at 20°C and 25°C. The fillings were evaluated on:

Hardness

The STA-hardness of the fillings was determined after one day storage at 20°C and 25°C. The results were:

Method: Cone : 60-

Depth : 2 mm

Speed : 0.5 mm/sec

20°C: Filling 1: < 2 gr

Filling 2: 32 gr

25°C : Filling 1 : < 2 gr

Filling 2: 12 gr

Sensory evaluation

The fillings were evaluated by the taste panel after storage at 20°C.

Filling 2 was much harder than filling 1. Filling 2 had a slightly slower and lower flavour release probably because it was harder.

Conclusion |

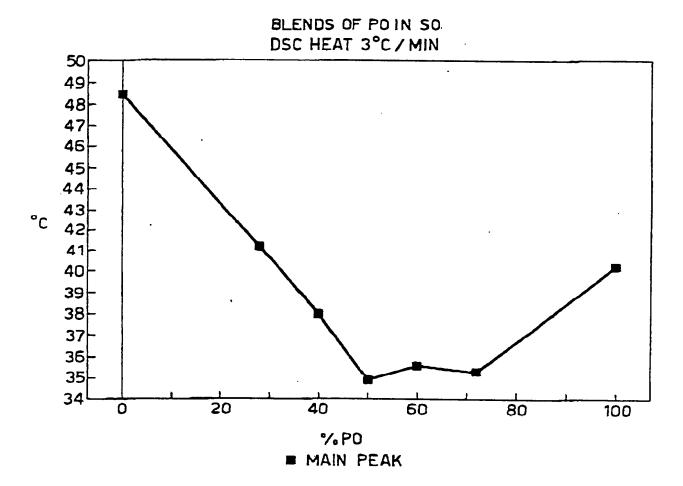
Although the SAFA content of the diglyceride based filling was lower, the product was much harder and had better body.

CLAIMS

- Fat blends, suitable for food products, comprising: 1. 10-60 wt%, preferably 30-55 wt% of diglycerides (= A) and 90-40 wt% of triglycerides (= B) wherein (A) contains at least 70 wt% of diglycerides of the SU-type (S= saturated fatty acid C12-C24; U= unsaturated fatty acid C16+), including high melting diglycerides (= C) with a melting point above 40°C, while (A) simultaneously contains at least one other fatty component (D), which fatty component (D) is selected, so that the melting point of the mixture (C+D) is at least 5°C less than the melting point of component (C), and wherein the triglyceride component (B) has a solid fat content (NMR-pulse, not stabilised) at 5°C of at most 40 ($N_s \le 40$), preferably at most 25, most preferably at most 15, while the total blend has a content of saturated fatty acids (= SAFA) of less than 40 wt% and an N_{35} < 15.
- 2. Fat blends according to claim 1, wherein the higher melting diglyceride (= C) is StO or PO (St= stearic acid, P= palmitic acid, O= oleic acid).
- 3. Fat blends according to claims 1-2, wherein the higher melting diglyceride (= C) is present in the diglyceride component (A) for at least 5 wt%, preferably at least 10 wt%.
- 4. Fat blends according to claims 1-3, wherein the other fatty component (D) is a diglyceride of the SU-type, which is different from the higher melting diglyceride (C).
- 5. Fat blends according to claims 1-4, wherein diglyceride (C) is StO and diglyceride (D) is PO,

which are present in diglyceride mixture (A) in a ratio of 80:20 - 20:80.

- 6. Fat blends according to claims 1-5, wherein the diglyceride component is the product of glycerolysis of a triglyceride mixture, rich in S_2U -triglycerides, followed by a monoglyceride removal and a fractionation.
- 7. Fat blends according to claims 1-6, wherein parts of the triglycerides (B) can be selected from the group, consisting of: sunflower oil, soybean oil, safflower oil, olive oil, maize oil, high oleic sunflower oil, high oleic safflower oil and olein fractions of vegetable oils.
- 8. Fat blends according to claims 1-7, wherein the diglycerides (A) and triglycerides (B) are free of trans fatty acid residues and free of chemically interesterified fats.
- 9. Food products, selected from the group consisting of: filling fats, enrobed filling fats, confectionery products, wrapper spreads, wrapper margarines, wrapper shortenings, tub spreads, tub margarines, cream alternatives, bakery products, doughs, cheese, mayonnaise and dressings, which products comprise a fat phase, wherein the fat phase at least partly consists of the fat blend according to claims 1-8.



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INTERNATIONAL SEARCH REPORT

Inter and Application No PCT/EP 95/00386

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